Article type: Communication

Compelling Rejuvenated Catalytic Performance in Metallic Glasses

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Keywords: metallic glasses, catalytic rejuvenation, crystallization, grain boundary, electron transfer

Metallic glasses (MGs) with the metastable nature and randomly atomic packing structure have attracted large attentions in catalytic family due to their superior catalytic performance. In contrast, their crystalline counterparts are restricted by the highly-ordered packing structure, less surface active sites, and crystallographic defects for catalytic activity. The uncertainty of different catalytic mechanisms and the intrinsic characteristics correlated to MGs and crystalline counterparts become a major impediment to promote their catalytic efficiencies and widespread applications. Herein, we report that the excellent catalytic behavior in Fe-based MGs goes through a detrimental effect with the partial crystallization,
but receives a compelling rejuvenation in the full crystallization. Further investigation reveals that multiphase intermetallics with electric potential differences in fully crystallized alloys facilitates the formation of self-motivated galvanic cells. More importantly, extensively reduced grain boundaries due to grain growth greatly weakens electron trapping and promotes inner electron transportation. The relatively homogenous grain-boundary corrosion in the intermetallics contributes to well-separated phases after reactions, leading to refreshment of surface active sites, thereby fast activating hydrogen peroxide and rapidly degrading organic pollutants. The exploration of catalytic mechanisms in crystalline counterparts of MGs provides significant insights into revolutionize novel catalysts.

Unlike crystalline alloys with a long-range highly ordered atomic packing structure, the atomic arrangements in metallic glasses (MGs) or amorphous alloys still remain mysterious at present.\(^1\)\(^-\)\(^5\) Owing to their unusual atomic formation during rapid solidification, MGs have many fascinating properties which induce an intense curiosity on their fundamental studies (e.g. basic structural model, glass transition, supercooling and glass forming ability, and thermal stability, etc.).\(^6\)\(^-\)\(^9\) Specially, enormous advances have been made in the use of MGs as structural engineering materials according to physical and mechanical properties (microscanner,\(^10\) and gears system,\(^11\) etc.). In addition, many encouraging results have been achieved in advanced functional properties, such as MgZnCa MGs as biodegradable implants because of extended solubility and good compatibility,\(^12\) FeCoSiB MGs as energy harvesting devices attributed to high magnetostriction,\(^13\) and PtCuNiP glassy nanowires as electrochemical devices ascribed to outstanding durability.\(^14\) Recently, there have been significant developments of MGs in the functional applications as catalysts, demonstrating far greater efficiency than crystalline catalysts. For example, FeSiBNb MG powder fabricated by ball milling is firstly applied in wastewater treatment and it exhibits 200 times faster
degradation performance than crystalline iron powder;[5] PdNiCuP glassy ribbons suggest a higher efficiency and a stronger stabilizing behavior in water splitting than commercial Pt/C catalyst;[4] FeSiB glassy ribbons activate peroxides with 5–10 times faster than other Fe-based catalysts.[12] The current research on MG catalysts mainly focuses on the alteration of atomic components,[15] the regulation of surface morphology,[5, 16] the promotion of electron motion,[15, 17, 18] etc. However, introducing crystals in MGs is lack of study on advanced catalytic behavior and usually considered to be impeditive in catalytic application.[18-22]

MGs were used to be simplified as glass constituted with atoms and their deformation behavior has a close correlation with their relaxation spectra.[23] During the isothermal treatment, MGs tend to reach the thermodynamic equilibrium (lower energy state) from the metastable state, interpreted as structural relaxation or aging,[5] and apparent structural variation occurs at or higher than the crystallization temperature leading to fast crystallization in a short time. MGs relaxing to lower energy states usually obtain undesirable properties, such as annealing-induced abrupt embrittlement,[24] transition from anelasticity to plasticity,[25] decreasing magnetic permeability,[26] and so on. Because of this, further crystallization behavior may be more attractive and is of significant for studying the mechanism of crystal nucleation and growth, and the unexpectedly advanced properties of crystals. For example, nanocrystals and their grain boundaries are found to be effective in altering the mechanical properties of materials, such as superior strength-ductility combinations by gradient microstructure from micro- to nano-scale crystallite due to suppression of strain localization[27] and enhancement of surface hardness and structure stability by low-angle grain boundaries in nanocrystals.[28] It is reported that twinned nanocrystals coupling with freestanding sub-nanometer clusters provide active hydrogen production sites and effectively optimize the photocatalytic hydrogen production.[29] Indeed, crystallization presents many novel advantages in catalytic fields (e.g. controllable crystal
structure, tunable surface and interfacial structures, and formation of galvanic cells, etc.). However, the relaxed behavior and further crystallized products in MGs for catalytic advance have not yet been systematically investigated and its mechanism is still not clear.

It is known that electron transfer is usually involved in catalysis with multistep reactions. That is, a catalysis usually occurs accompanied with addition/removal of electrons throughout the processes. However, the ubiquitous fact leads to easily omit the important role of electrons as an efficient catalyst in catalytic activities. Therefore, developing catalysts that are fast and efficient, to some extent, is a way to exploit fast electron-transfer materials. According to our previous work in MGs, the weak bonding of randomly arranged atoms in MGs makes a significant contribution to activation, resulting in a stronger electron-transfer ability and a superior catalytic performance compared to other crystalline materials.

However, the advanced catalytic application of crystals in Fe-based crystallized MGs is nearly absent. Herein, we present two Fe-based glassy ribbons with atomic components of Fe$_{78}$Si$_{9}$B$_{13}$ and Fe$_{73.5}$Si$_{13.5}$B$_{9}$Cu$_{1}$Nb$_{3}$ under different ranges of annealing temperatures to systematically investigate the effects of crystallization, grain growth, grain boundaries and atomic components induced alteration of phase on the catalytic performance of MGs. The compelling evidences of the formation of self-motivated galvanic cells from intermetallics and the reducing grain boundaries contributing to fast electron transfer provide an important insight into the role of crystallized MGs in wastewater treatment.

Figure 1 shows the electron microscopic images of the as-received and annealed Fe$_{78}$Si$_{9}$B$_{13}$ and Fe$_{73.5}$Si$_{13.5}$B$_{9}$Cu$_{1}$Nb$_{3}$ ribbons. The homogeneous amorphous matrix in the as-received Fe$_{78}$Si$_{9}$B$_{13}$ ribbons (Fe-AR) is indicated in Figure 1a. As shown in Figure 1b, the Fe$_{78}$Si$_{9}$B$_{13}$ glassy ribbons annealed at 450°C (Fe-A450) present a trace of nanocrystalline α-Fe(Si) formation with an average grain size ~5 nm, however, the main amorphous nature is well maintained (inset of Figure 1b). This result is in agreement with X-ray diffraction...
(XRD) and different scanning calorimetry (DSC) analysis with the main amorphous feature (Figure S1, Supporting Information). Figure S1a in the Supporting Information shows that two distinct peaks are associated with the crystallization behavior of $\alpha$-Fe(Si) and stable $\alpha$-Fe(Si) + Fe$_2$B eutectic in Fe$_{76}$Si$_9$B$_{13}$, respectively.$^{[33]}$ Since a closer gap exists between the two crystallization peaks, the crystal phase transition of Fe$_{78}$Si$_9$B$_{13}$ glassy ribbon is more sensitive to temperature variation than the Fe$_{73.5}$Si$_{13.5}$B$_9$Cu$_1$Nb$_3$ glassy ribbon (Figure S1b, Supporting Information). As a result, $\alpha$-Fe(Si) dendrites start to appear from the amorphous matrix as the main crystalline product at 520°C, while $\alpha$-Fe(Si) + Fe$_2$B eutectic nucleates rapidly on primary dendrite at 560°C (Table S1, Supporting Information). However, a residual amorphous phase is still observed at an annealed temperature of 600°C (Fe-A600) in Figure 1c, where the corresponding selected area electron diffraction (SAED) indicates the existence of $\alpha$-Fe(Si) and Fe$_2$B. Further increasing the annealed temperature to 750°C (Fe-A750) would lead the residual amorphous phase to be fully crystallized with a distinct and irregularly-shaped grain boundary (Figure 1d). The corresponding inset is a high-resolution transmission electron microscopy (HRTEM) image at the grain boundary of the two phases, where Fe$_2$B is isolated from previous eutectic. Figure 1e shows that grain sizes of $\alpha$-Fe(Si) and Fe$_2$B have grown to ~994 nm and ~771 nm, respectively, at the high annealing temperature of 900°C (Fe-A900). The grain sizes of crystalline phases in Fe$_{78}$Si$_9$B$_{13}$ ribbons are summarized in Table S2 (Supporting Information). Insets of Figure 1e individually demonstrate well-separated lattice structures of $\alpha$-Fe(Si) and Fe$_2$B. On the other hand, Figure 1f,g illustrates similar results for the as-received Fe$_{73.5}$Si$_{13.5}$B$_9$Cu$_1$Nb$_3$ ribbons (FeCu-AR) and at annealed temperature of 450°C (FeCu-A450) compared to Fe$_{78}$Si$_9$B$_{13}$ ribbons. Compared to Fe$_{78}$Si$_9$B$_{13}$ glassy ribbon, the crystallization behavior of Fe$_{73.5}$Si$_{13.5}$B$_9$Cu$_1$Nb$_3$ ribbon can be clearly divided into two stages due to a wide range of transition (Figure S1b, Supporting Information). Two phases of $\alpha$-Fe(Si) and Fe$_2$B are firstly formed and the Fe$_{16}$Nb$_6$Si$_7$ phase
shows up after the second crystallization. Figure 1h shows the formation of well-separated α-Fe(Si) and Fe₂B with lattice spacing of 0.20 nm at (110) plane and of 0.21 nm at (002) plane, respectively, at an annealing temperature of 600°C (FeCu-A600). The calculated grain sizes of α-Fe(Si) and Fe₂B from XRD analysis are 10 nm and 12 nm, respectively, which is consistent with the TEM observations. The residual amorphous matrix is observed by enveloping the two phases. Figure 1i displays the full crystallization of Fe₇₃.₅Si₁₃.₅B₉Cu₁₁Nb₃ ribbons at an annealing temperature of 800°C (FeCu-A800) and Figure 1j is the corresponding HRTEM, showing the α-Fe(Si) phase with a lattice spacing of 0.20 nm indexed as plane (110) and Fe₁₆Nb₆Si₇ phase with a lattice spacing of 0.65 nm at (111) plane. In addition, compared with α-Fe(Si) phase, the HRTEM image with corresponding EDS analysis of Fe₂B phase in Figure S2 shows specific features of multiple stacking faults and annealing twins in FeCu-A800, which is consistent in Figure 1h. Further annealing ribbons to 950°C (FeCu-A950) appears to significant growth in each phase (Figure 1k). The observed internal microstructure evolution indicates an initially partially crystallized and further fully crystallized behaviors under thermal treatment in MGs leading to transformation from amorphous to full crystallized state, which would have a significant impact on the corresponding catalytic behavior.

The engineering of surface morphology is one of the most effective ways to investigate the catalytic mechanism in heterogeneous catalysis. Figure 2a-e and 2f-j shows the scanning electron microscopy (SEM) images of Fe₇₈Si₁₀B₁₃ and Fe₇₃.₅Si₁₃.₅B₉Cu₁₁Nb₃ ribbons, respectively. As shown in Figure 2a,f, the surfaces of the as-received ribbons are very smooth. Simultaneously, the surface of the as-annealed samples under low-temperature annealing (350–600°C) present similar smooth surface morphologies (see Figure S3 in the Supporting Information). Then incompactly crystallized α-Fe(Si) starts to precipitate and aggregate on the Fe₇₈Si₁₀B₁₃ and Fe₇₃.₅Si₁₃.₅B₉Cu₁₁Nb₃ ribbon surfaces at annealed
temperatures above 600°C,[18] as shown in Figure 2b,g. The α-Fe(Si) on the surface serves as a nuclei and facilitates the agglomeration of Fe-rich oxides after prolonged contact with air. Then further expansion of aggregates occurs at 750 °C and 800°C (Figure 2c,h) due to a stronger nucleation rate. The dense spheroidal particles are observed on both Fe-based ribbon surfaces at ~900°C (Figure 2d,e,i,j). Surface morphologies under progressive annealing temperatures indicate that the internal nucleation and grain growth significantly improve the formation of Fe-rich aggregates on surfaces, which could possibly facilitate higher surface reactivity and faster electron transfer.

Figure 2k,l shows the atomic force microscopy (AFM) images of Fe-A900 and FeCu-A950 ribbons. Large spheroidal aggregates can be seen with maximum surface fluctuation of Fe-A900 under 0.41 μm and of FeCu-A950 under 0.52 μm. The root-mean-square roughness of Fe-A900 surface is measured as 21.1 nm compared to FeCu-A950 of 94.9 nm, indicating more nuclei and aggregates are formed on the FeCu-A950 surface. Owing to the nucleation and grain growth at high annealing temperatures, the crystallized ribbons should have greater surface roughness than amorphous ribbons.

The elemental analysis and atomic chemical state of ribbons are characterized by X-ray photoelectron spectroscopy (XPS) (Figure 2m-r). A mixture of Fe⁰ (706.0 eV, 705.9 eV/706.6 eV), Fe²⁺ (709.7 eV) and Fe³⁺ (711.5 eV, 711.0 eV) coexists at Fe-AR and FeCu-AR (Figure 2o,r) with relative contributions of Fe⁰ as 21.7% and 28.4%, respectively. In addition to the peak analysis of O 1s (Figure S4a,d, Supporting Information), the thin film SiO₂ and Fe oxides (i.e. FeOₓ, Fe₂O₃ and FeOOH) are confirmed on the surface.[35] Then all Fe atoms on the surface of Fe-A600 (maximum at peak intensity) transfer to Fe²⁺ (709.6 eV, assigned to FeOₓ)[36] and Fe³⁺ form (710.7 eV and 712.7 eV, assigned to Fe₂O₃ and FeOOH)[37, 38] while the spectrum of Fe 2p declines to a weak signal at Fe-A900, where an almost full coverage by SiO₂ layer can be seen in Figure S4c (Supporting Information). Noting the gradual increase
of Si 2p peak in all processes, Si atoms tend to highly diffuse and cover the ribbon surface at high annealing temperatures and Fe atoms are thereby undetectable. On the other hand, Fe⁰ has fully transformed to Fe²⁺ (709.5 eV) and Fe³⁺ (710.7 eV and 712.5 eV) at FeCu-A550 (Figure 2p,36-38), which is the same as Fe-A600. The Fe 2p signal is undetected at FeCu-A690. The gradual increase of Si spectra indicates that oxides of Si are also formed and fully covered on ribbon surface (Figure S4f, Supporting Information), and the Si atoms have a faster diffusion rate to the surface of Fe₇₃.₅Si₁₃.₅B₉Cu₁Nb₃ ribbons compared to Fe₇₈Si₉B₁₃ with the same annealing temperature.

**Figure 3a,b** investigates the variation of catalytic ability in the Fenton-like process of Fe₇₈Si₉B₁₃ and Fe₇₃.₅Si₁₃.₅B₉Cu₁Nb₃ ribbons from glassy to fully crystallized states and Figure S5 (Supporting Information) shows the effects of experimental parameters on both glassy and crystallized states. Progressive annealing treatment leads to a significant reduction on catalytic ability from fully glassy state (Fe-AR and FeCu-AR) to partially crystallized (Fe-A600 and FeCu-A690). A sudden increase is observed at Fe-A750 and the fast degradation almost achieves a close reaction rate ($k = 0.258 \text{ min}^{-1}$, Figure S6, Supporting Information) at Fe-A900 compared with glassy state. Compared with Fe₇₈Si₉B₁₃, the efficiency decay due to incipient crystallization is far more prominent for Fe₇₃.₅Si₁₃.₅B₉Cu₁Nb₃ with the lowest degradation rate at FeCu-A550 (Figure 3b), followed by a dramatic increase from $k = 0.003 \text{ min}^{-1}$ at FeCu-A550 to $k = 0.111 \text{ min}^{-1}$ at FeCu-A950. Kinetic studies indicate a close correlation between surface adsorption and degradation efficiency (Figure S6, Supporting Information), while Table S3 (Supporting Information) systematically investigates $k_{SA}$ (essential degradation ability) of as-received and annealed ribbons in this work and compared with other MGs. However, the fast catalytic behavior induces a relatively higher Fe leaching in the solution (Figure 3c). The total organic carbon (TOC) removal rate (Figure 3d) and progressive change of UV-vis spectra (see Figure S7 in the Supporting Information)
demonstrate the fast generation of reactive •OH leading to the complete breakage of dye structures with conversion to environmental friendly CO₂, H₂O, etc.\textsuperscript{17}

The electron transfer of material usually benefits from its unique structure (e.g. unstable out-sphere electron, galvanic cell, etc.),\textsuperscript{39} which induces various surface morphologies after dye degradation but with a strong stability of internal structure (Figure S8, S9a,d and S10, Supporting Information). As such, Figure 3e-g studies the role of electron transfer in the catalytic behavior of ribbons. Figure 3e depicts open circuit potential (OCP) that an initial shift to less noble potential occurs at all ribbons of Fe-A900 (-0.67 V\textsubscript{SCE}), Fe-AR (-0.64 V\textsubscript{SCE}), Fe-A600 (-0.61 V\textsubscript{SCE}) and FeCu-A950 (-0.54 V\textsubscript{SCE}) due to the progressive dissolution of native oxide layers.\textsuperscript{40} However, both FeCu-AR and FeCu-A550 are positively shifted to -0.42 V\textsubscript{SCE} and -0.33 V\textsubscript{SCE}, respectively, showing cathodic processes owing to the formation of passive film.\textsuperscript{18} These facts indicate that Fe-AR and Fe-A900 have less surface stability with a fast electron transfer compared with the strong anticorrosion characteristics in FeCu-AR and FeCu-A550.\textsuperscript{18} Figure 3f shows potentiodynamic polarization curves with the identical samples in OCP after stabilization, suggesting superior resistance to localized corrosion because of the anodic behaviors of ribbons without breakdown potential. A lower corrosion potential is achieved in Fe\textsubscript{78}Si\textsubscript{9}B\textsubscript{13} than in Fe\textsubscript{73.5}Si\textsubscript{13.5}B\textsubscript{9}Cu\textsubscript{1}Nb\textsubscript{3} ribbons, suggesting a higher occurrence of oxidation reactions; that is, stronger surface reactivity and fast electron transfer in Fe\textsubscript{78}Si\textsubscript{9}B\textsubscript{13} ribbons. Figure 3g shows electrochemical impedance spectroscopy (EIS) spectra at a frequency range from 100 kHz to 0.01 Hz. The larger capacitive loops in Fe-A600 and FeCu-A550 (attributed to charge-transfer processes) reveal that the partial crystallization significantly improves corrosion resistance.\textsuperscript{40} In addition, the second semicircles of fully crystallization samples (Fe-A900 and FeCu-A950) are similar in size to the semicircles for Fe-AR and FeCu-AR with less impedance, indicating that a fast electron transfer occurs in the fully crystallized ribbons.
Based on the structural evolution and the performance in the catalytic degradation of materials, Figure 3h,i suggests that the catalytic behavior of Fe-based crystallized ribbons is affected by the crystallization rate and the average grain size ($D$). It has clearly revealed a prominent reduction in the catalytic ability of ribbons at the initial crystallization (as represented by the transition from a metastable to a stable state). As it is close to full crystallization (as represented by the formation of grain boundary and grain growth), the grain size dominates the reaction rate.

Previous reports indicate that although a long-term stability exists in MG catalysts (strong reusability), the catalysts usually show a lower catalytic ability when increasing the reused times.\cite{15,19,41} However, the interesting findings in reused experiments (Figure 4a,b and corresponding insets), especially for Fe-A900 ribbons, suggest that the degradation efficiency for the 1st used crystallized ribbons is not their intrinsic catalytic behaviors and the fully crystallized ribbons at high annealing temperature are expected to exhibit stronger catalytic abilities than the existing form. Accordingly, the surface layer of Fe-A900 ribbons after reaction is easily detached, leading to a large-scale layer shedding after reutilization and ultrasonic vibration (Figure S9a,b, Supporting Information). The zoom-in view (Figure 4c) indicates that the flocculent-like materials are the after-reacted sediments from MB degradation. Those sediments are removed after ultrasonic cleaning and there are irregularly granular materials distributing loosely on the 2nd used Fe-A900 ribbon surface (Figure 4d). The surface morphology of 5th used Fe-A900 shows that the irregularly granular materials with light color are embedded in the ribbon surface and surrounded by other larger grains (Figure 4e). Note that those grains have granular sizes of less than 1 μm, matching the average grain size measurements of α-Fe(Si) (~1 μm) and Fe$_2$B (~800 nm) in Fe-A900 ribbons (Table S2, Supporting Information). On the other hand, a limited layer shedding occurs at the 1st used FeCu-A950 ribbons (inset of Figure S9d, Supporting Information) and
an ultrasonic vibration of 2nd used FeCu-A950 ribbons results in a negligible surface variation (Figure S9e, Supporting Information). The surface layer fragments are eliminated and only a small amount of residual flocculent-like products remain on the surface (Figure 4f, g). Further reusing FeCu-A950 ribbons shows a gradual increase of surface layer shedding (Figure S9f, Supporting Information) and a clear surface texture buried under the layer (Figure 4h). Similarly, those grains under surface layer have a good agreement with average grain size as α-Fe(Si) (~500 nm), Fe2B (~500 nm) and Fe16Nb6Si7 (~250 nm) in FeCu-A950 ribbons (Table S2, Supporting Information).

Current understanding on metallic glasses of corresponding crystallized counterpart is limited to the decay of catalytic activity in wastewater remediation due to structural relaxation and partial crystallization.[18-22] On this basis, however, it is apparent that full crystallization with the generation of different intermetallics in Fe-based ribbons induces a rapid rejuvenation of catalytic efficiency when H2O2 activation takes place, leading to the fast degradation of organic pollutants. This fact demonstrates that amorphous materials in atomic scale are not the only form which is favorable for fast peroxide activation. In this work, although amorphous structure is detected at the initial annealing, temperature-driven transition of relaxation induces an increase of activation energy (α-relaxation),[23] which subsequently greatly inhibits catalytic ability of glassy ribbons (green curves in Figure 3a, b). A fast crystallization after the onset of crystallization temperature then results in primary α-Fe(Si) nucleation and growth (increase of volume fraction Vf) with the existence of Fe2B (Table S1, Supporting Information).[33, 42] However, α-Fe(Si) and Fe2B phases are enveloped by the amorphous matrix at the partially crystallized stage. At this point, an extremely low catalytic performance of partially crystallized ribbons occurs. Then the eutectic crystallization products of Fe73Si13.5B13 are further nucleated and isolated from each other while α-Fe(Si) and Fe2B in Fe73.5Si13.5B0Cu1Nb3 are separated from the amorphous matrix faster.
Increasing annealing temperature facilitates the grain growth with a distinct boundary and the contact between different crystalline phases, forming micro-sized galvanic cells due to their potential difference. As the full crystallization is achieved, all the phases with distinct boundaries then grow into larger grains by consuming the surrounding boundaries until they come in contact with different phases. On this basis, a schematic illustration is shown in Figure 5 (bottom left). Given that multiphase intermetallics with potential difference easily induce self-motivated galvanic cells, a grain-size evolution correlated with grain boundary becomes an important clue in this work. The size dependence of electrical resistivity of grain has been widely investigated. A grain boundary plays a significant effect on electrical resistivity in the grains with nanometer length-scale. This can be verified by a relation of resistivity and annealing temperature, where annealed ribbons generate nano-sized grains with high resistivity. It is also consistent with our result of catalytic behavior that the lowest catalytic efficiency of crystallized ribbons locates at samples Fe-A600 and FeCu-A550, indicating the catalytic behaviors of partially and fully crystallized ribbons are an electron-transfer dominated process in addition to a correlation with grain size. From a viewpoint of grain boundary phenomena, an increase of electrical resistivity can be attributed to a significant electron scattering effect at the grain boundary. In this work, grain sizes of those partially crystallized ribbons approximate to < 50 nm and an increase in volume fraction of crystalline phases at the partially crystallized ribbons creates a very large grain boundary per unit area, which has a strong electron trapping effect and acts as barriers for electron transportation. As a result, a low transportation efficiency of electron occurs at the partially crystallized ribbons. On the other hand, the grain size has a dramatic increase by at least an order of magnitude after fully crystallized (Table S2, Supporting Information), leading to an apparent decrease in grain boundary per unit area, which apparently reduces barriers and facilitates electrons transporting in the grains. In
addition, as demonstrated in multiphase galvanic cells and conductors,\textsuperscript{[50-53]} it is highly possible for electrons transferring across the grains (bottom right in Figure 5), which are the dominant electron donors, although they need to overcome grain boundary barrier (higher potential) to achieve further transportation. For Fe-A900 ribbons, a high catalytic efficiency is attributed to not only a large grain size with less grain boundary, but also a homogenous distribution of two phases (\(\alpha\)-Fe (Si) and Fe\(_2\)B), thereby facilitating electron transportation across the grain boundaries. However, the electron transfer is limited at the local structure, leading to initially localized corrosion (Figure S9b, Supporting Information), but further reaction tends to homogenize and activate all reaction sites (Figure S9c, Supporting Information). In addition, the electronic conductivity of multiphase should be considered with an involvement of additional phase, especially for the newly generated Fe\(_{16}\)Nb\(_6\)Si\(_7\) phase in fully crystallized Fe\(_{73.5}\)Si\(_{13.5}\)B\(_9\)Cu\(_1\)Nb\(_3\) ribbons in this work, which presents as a little variation of catalytic performance when the annealing temperature increases from 690 to 800\(^\circ\)C although the grain size has apparently increased. With a smaller grain size due to the refinement function of Cu and a relatively discrete distribution of grains, FeCu-A950 ribbons exhibit a lower catalytic ability than Fe-A900 ribbons. According to the aforementioned discussion, it is reasonable to believe that the generated intermetallics with electric potential difference serve as self-motivated galvanic cells and a grain growth with an extensively reduced grain boundary plays a pivotal role in fast electron transfer and in the Fenton-like reaction.

On the other hand, electrons cannot achieve migration without a correlation of electron carrier and transportation.\textsuperscript{[54]} Other than internal structural evolution, surface topology remains as a possible reason for the difference between glassy and crystallized ribbons. In this work, due to a higher contribution of coordinately unsaturated Fe\(^0\) on the surface of as-received ribbons (Fe-AR and FeCu-AR), the Fe\(^0\) greatly facilitates the electron transfer in the
heterogeneous catalysis leading to a high surface reactivity. Although the coverage of SiO$_2$ results in a loss of Fe$^0$ on the surface, it is found that self-motivated galvanic cells caused by high-temperature annealing-induced multiple phases (Fe-A900 and FeCu-A950) can make up the absence of electrons in Fe$^0$, which can retain a high efficiency of electron transfer. Comparative studies (Figure 2a-j) show that microscopic irregularities in the surface become noteworthy in the high-temperature annealed surface due to the subsequent nucleation of $\alpha$-Fe(Si) on the surface.\textsuperscript{[18]} For nucleation on the surface, crystallized Fe atoms need to reach the substrate and diffuse along the surface until they form nuclei. The formed nuclei further capture and react with oxygen to produce large aggregates (FeO$_x$, Fe$_2$O$_3$ and FeOOH, etc.), after prolonged contact with air leads to actual grain size on the surface being larger than the microstructure (top left in Figure 5). An electron transfer originates from a tendency for losing electron from crystallized Fe products when activating H$_2$O$_2$. The densely packed $\alpha$-Fe(Si) is firstly consumed in contact with H$_2$O$_2$ to form Fe$^{2+}$, after which hollow precipitates are observed (Figure S9a,b, Supporting Information). With the consumption of surface-aggregated $\alpha$-Fe(Si), H$_2$O$_2$ has an opportunity to further permeate to reach crystallized phases under the surface protection. It is easy to separate the protected layer of the ribbon surface due to internal consumption of $\alpha$-Fe(Si), leading to layer shedding and extensive exposure of galvanic cells to the MB dye and H$_2$O$_2$. This is further confirmed by the surface morphologies of Fe-A900 ribbons after reutilization. Apparently the catalytic enhancement of 2$^{nd}$ used Fe-A900 ribbons is mainly attributed to easily detached surface layer, leading to a re-exposure of multiphases ($\alpha$-Fe(Si) and Fe$_2$B). As multiphase galvanic cells are reused in the catalytic activities, they can directly contact with H$_2$O$_2$ and be rapidly activated, providing abundant active sites and leading to the fast electron transfer. Regardless of the oxide layer on the Fe-A900 ribbon surface, the reused ribbons can better elucidate the rejuvenated catalytic behavior at the high annealing temperature (top right in Figure 5), where
the 2nd used Fe-A900 have been demonstrated to have a catalytic performance as high as their MG counterparts. The kinetic study also suggests a process of surface adsorption and corrosion by dye molecules and H$_2$O$_2$ within 2 to 5 min (Figure S6h, Supporting Information), leading to a lower efficiency of Fe-A900 for surface activation, which is responsible for the lower efficiency of Fe-A900 at the 1st use. In comparison with a lower enhanced catalytic ability in FeCu-A950 ribbons after reutilization, it is found that there is a stronger binding between phases (α-Fe(Si), Fe$_2$B and Fe$_{16}$Nb$_6$Si$_7$) and surface layer due to the additive Nb. The stronger surface stability in Fe$_{73.5}$Si$_{13.5}$B$_9$Cu$_1$Nb$_3$ glassy ribbons has been retained even if their structures have a transformation from amorphous to crystalline. The minor layer shedding indeed provides limited promotion of contact between exposed phases and H$_2$O$_2$, thereby leading to an undesirable enhanced degradation efficiency. Notably, surface morphologies of 5th reused ribbons (Figure 4e,h) indicate that an apparent corrosion after elimination of surface layer occurs along with the grain boundary. The relatively homogenous grain-boundary corrosion due to a high concentration of electrons at the grain boundaries in Fe-A900 contributes to well-separated phases after reactions while the grain boundary in FeCu-A950 becomes clearer but their corrosions concentrate on restricted phases resulting in surface collapse at the specific area. The residual phases in FeCu-A950 ribbons act as another layer inhibiting further diffusion of H$_2$O$_2$ and the catalytic ability decreases after continuous reutilization.

In summary, with a systematic understanding structural and surface evolution in two comparable Fe-based metallic glasses (Fe$_{78}$Si$_9$B$_{13}$ and Fe$_{73.5}$Si$_{13.5}$B$_9$Cu$_1$Nb$_3$) under annealing treatment, a formation of self-motived galvanic cells from intermetallics suggests a significant clue of rejuvenated catalytic behaviors in fully crystallized ribbons from MGs. Further investigation demonstrates that the grain growth with extensively reduced grain boundary dominates a fast electron transfer, leading to fast activation efficiency for H$_2$O$_2$. 

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The related phenomena have also been found in the other Fe-based metallic glasses. The present findings demonstrate a distinct catalytic mechanism between MGs and fully crystallized counterparts. Since not all the materials are achievable in amorphous state, it provides an effective way by controlling grain size, grain boundary and potential-difference phases for exploiting novel crystallized catalysts.

Experimental Section

Materials Preparation and Characterization: Glassy ribbons with nominal composition of Fe$_{78}$Si$_9$B$_{13}$ and Fe$_{73.5}$Si$_{13.5}$B$_9$Cu$_1$Nb$_3$ (see Preparation of glassy ribbons, Supporting Information) were firstly cut into pieces. The glassy ribbons with ~6 g for each time were subjected to thermal treatment at a heating rate of 20°C min$^{-1}$ in a tube furnace (OTF-1200X, Hefei Kejing Materials Technology Co., Ltd.). The thermal treatment lasted for 5 min at the specified temperature followed by fast air-cooling in the tube furnace. Operations for all ribbons in the tube furnace were protected by Argon gas to avoid oxidation. The annealing temperatures, ranging from 350°C to 950°C, were selected as three stages according to the onset crystallization temperature, the first and second peak of crystallization in DSC traces: (1) amorphous state: before the onset crystallization temperature (350 and 450°C for both Fe-based glassy ribbons); (2) partial crystallization: between the first and second stage of crystallization (520, 560 and 600°C for Fe$_{78}$Si$_9$B$_{13}$, and 550, 600 and 690°C for Fe$_{73.5}$Si$_{13.5}$B$_9$Cu$_1$Nb$_3$); (3) full crystallization: after the second stage of crystallization (750 and 900°C for Fe$_{78}$Si$_9$B$_{13}$, and 800 and 950°C for Fe$_{73.5}$Si$_{13.5}$B$_9$Cu$_1$Nb$_3$). The annealed samples of Fe$_{78}$Si$_9$B$_{13}$ ribbons were denoted as Fe-Axxx, for example Fe-A350 in 350°C, while the samples in Fe$_{73.5}$Si$_{13.5}$B$_9$Cu$_1$Nb$_3$ were denoted as FeCu-Axxx. Both as-received ribbons were denoted as AR. The structural features and phase identification of samples were characterized by XRD recorded on a PANalytical Empyrean diffractometer with Cu-K$_\alpha$ radiation ($\lambda$ =
A differential scanning calorimeter (Netzsch DSC-404C) at a heating rate of 20°C min\(^{-1}\) was used to analyze thermal behavior and physical parameters (i.e. onset crystallization temperature \(T_x\) and crystallization temperature \(T_p\)). The microstructures and crystallization processes of as-received and annealed samples were investigated by TEM (JEOL JEM-2100). The surface morphology and the surface roughness of samples was observed by SEM (FEI Verios 460) and AFM (Dimension 3000 Scanning Probe Microscope). Chemical states of elements on the surface were investigated by XPS using a Kratos AXIS Ultra DLD instrument with Al-Kα X-ray.

**Evaluation of grain size:** The average grain sizes of \(\alpha\)-Fe(Si), Fe\(_2\)B, Fe\(_3\)Si and Fe\(_{16}\)Nb\(_6\)Si\(_7\) in annealed samples were estimated by two methods. For grain size 10 nm < \(D\) < 100 nm, Scherrer formula was applicable in XRD analysis.\(^{[18]}\)

\[
D = \frac{K\lambda}{\beta\cos\theta}
\]

(1)

where \(D\) is the mean grain size, \(K\) is a dimensionless shape factor, \(\lambda\) is the X-ray wavelength, \(\beta\) is the breadth at half the maximum peak intensity, \(\theta\) is the Bragg angle (in degrees). \(K\) is taken as 0.94 for spherical crystals with cubic symmetry in this work. Grain sizes larger than 100 nm were evaluated by the linear line segment drawn on the bright-field TEM micrographs described by the following Equations (2)-(4).\(^{[44]}\)

\[
L = NL
\]

(2)

\[
l = \frac{4}{3}R
\]

(3)

\[
D = \frac{3L}{2N}
\]

(4)

where \(L\) is the length of line segment, \(N\) is the number of grains on the line segment, \(l\) is the average length of one grain. A grain is regarded as a sphere with a mean radius of \(R\) in a three-dimensional space and thus the average grain size \(D\) can be calculated.
Electrochemical measurement: A Parstat 2273 electrochemical station in a traditional three-electrode cell was employed throughout all the electrochemical measurements. The as-received and annealed samples with an exposed surface area of ~1.0 cm² served as a working electrode while a platinum sheet and a saturated calomel electrode (SCE) were applied as the counter electrode and the reference electrode, respectively. The simulated HCl solution was adjusted to be pH 3.0. The OCP was measured for more than 10 h to achieve stabilization of samples. A sweep rate of 0.1667 mV s⁻¹ was performed within the range of −0.8 to +0.8 V in potentiodynamic polarization tests. EIS was investigated at the stabilized OCP potential with an AC amplitude of 5 mV over the frequencies ranging from 10⁵ to 10⁻² Hz.

Catalytic analysis: The catalytic performances of as-received and annealed glassy ribbons were investigated by the involvement of hydrogen peroxide (H₂O₂, 30 wt.%) for catalytic oxidation of methylene blue (MB) dye solution, which were supplied by Sigma-Aldrich and Xilong Chemical Co., Ltd. Other chemicals including Tert-butanol (TBA), hydrochloric acid (HCl), sodium hydroxide (NaOH), nitric acid (HNO₃), sodium nitrite (NaNO₂) were used at analytical grade without purification. Milli-Q water (18.2 MΩ·cm) was used throughout the experiments. All the reactions involving 20 ppm of MB solution, 0.5 g L⁻¹ pretreated glassy ribbons, 1.0 mM H₂O₂ and pH 3.0 were conducted in a thermostatic water bath to control the constant temperature (i.e. 25, 30, 40, 50, 60°C). The dye solution was stirred at a fixed speed of 300 rpm during the degradation process followed with sampling and characterization by UV–vis spectrometer (Perkin Elmer Lambda 35) at predetermined time intervals. The absorbance peak (λmax) of MB dye was measured to be 664 nm. In reused experiments, after used ribbons were washed by Milli-Q water for 3 times, and then immersed in the Milli-Q water with pH 3.0 for ultrasonic vibration (HWASHIN Powersonic 410, Hwashin Technology Co.) by 90 s. The after ultrasonically cleaned ribbons should be further washed for 3 times and employed for another reused experiment immediately to avoid further surface
oxidation. Fe leaching concentration was measured by the trace element analysis (iCAP Q ICP-MS, Thermo Fisher Scientific). Before ICP measurement, 2% v/v HNO₃ was used to dilute dye samples with filtration. Total organic carbon (TOC) was assessed by a TOC analyzer (TOC-VCSH, Shimadzu). An excessive NaNO₂ solution (0.1 M) was used to quench the reactions.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

Acknowledgements

Financial supports from the ECU Innovator Awards [Project No. 23641], Australian Research Council Discovery Project [DP130103592] and National Science Foundation of China (Grant Nos. 61671206, 51771103) are gratefully acknowledged.

Conflict of Interest

The authors declare no conflict of interest.

Received: ((will be filled in by the editorial staff))
Revised: ((will be filled in by the editorial staff))
Published online: ((will be filled in by the editorial staff))

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Figure 1. Microstructure revolution. a-e) TEM images of Fe$_{78}$Si$_{9}$B$_{13}$ at an as-received state and at annealing temperatures of 450°C, 600°C, 750°C and 900°C. f-k) TEM images of Fe$_{73.5}$Si$_{13.5}$B$_{9}$Cu$_{1}$Nb$_{3}$ at an as-received state and at annealing temperatures of 450°C, 600°C, 800°C, and 950°C. j) is HRTEM of i) at 800°C. All the insets are SAED patterns, except d) is HRTEM.
Figure 2. Surface characterization. a-d) SEM images of Fe$_{78}$Si$_9$B$_{13}$ at an as-received state and at annealing temperatures of 600°C, 750°C and 900°C. e) zoom-in view of SEM image at an annealing temperature of 900°C. f-i) SEM images of Fe$_{73.5}$Si$_{13.5}$B$_9$Cu$_1$Nb$_3$ at an as-received state and at annealing temperatures of 690°C, 800°C and 950°C. j) zoom-in view of SEM image at an annealing temperature of 950°C. k,l) AFM images of annealed Fe$_{78}$Si$_9$B$_{13}$ ribbon at 900°C and of annealed Fe$_{73.5}$Si$_{13.5}$B$_9$Cu$_1$Nb$_3$ at 950°C. m) Full range XPS spectra of Fe$_{78}$Si$_9$B$_{13}$ ribbons. n,o) High resolution XPS spectra of Fe$_{78}$Si$_9$B$_{13}$ ribbons. p) Full range XPS spectra of Fe$_{73.5}$Si$_{13.5}$B$_9$Cu$_1$Nb$_3$ ribbons. q,r) High resolution XPS spectra of Fe$_{73.5}$Si$_{13.5}$B$_9$Cu$_1$Nb$_3$ ribbons. The root-mean-square surface roughness of the annealed sample in an AFM image is calculated by taking the average at 4 contact points.
Figure 3. Catalytic and electrochemical behavior. a,b) Effects of annealing temperature on \( \text{Fe}_{78}\text{Si}_{9}\text{B}_{13} \) glassy ribbons and \( \text{Fe}_{73.5}\text{Si}_{13.5}\text{B}_{9}\text{Cu}_{1}\text{Nb}_{3} \) glassy ribbons against MB degradation rate (\( \frac{C}{C_0} \), where \( C \) is the dye concentration at time \( t \) and \( C_0 \) is the initial concentration). c,d) Fe leaching concentration towards surface reactivity and total organic carbon removal rate of selected glassy, partially crystallized and fully crystallized ribbons. Experimental conditions: dye concentration of 20 ppm, \( \text{H}_2\text{O}_2 \) concentration of 1.0 mM, catalyst dosage of 0.5 g L\(^{-1}\), \( \text{pH} \) 3.0, temperature of 25\( ^\circ \text{C} \). e-g) Open circuit potential as function of time, Potentiodynamic polarization curves and electrochemical impedance spectroscopy measurement of \( \text{Fe-AR}, \text{Fe-A600}, \text{Fe-A900}, \text{FeCu-AR}, \text{FeCu-A550} \) and \( \text{FeCu-A950} \) immersed in HCl solution (\( \text{pH} \) 3.0). h,i) Variation of methylene blue degradation efficiency towards crystallization rate and average grain size in \( \text{Fe}_{78}\text{Si}_{9}\text{B}_{13} \) and \( \text{Fe}_{73.5}\text{Si}_{13.5}\text{B}_{9}\text{Cu}_{1}\text{Nb}_{3} \) ribbons. The average grain size is measured by the corresponding contribution (volume fraction \( V_f \)) of each phase in the alloy system.
Figure 4. Intrinsic catalytic performance of reused Fe$_{78}$Si$_9$B$_{13}$ and Fe$_{73.5}$Si$_{13.5}$B$_9$Cu$_1$Nb$_3$ ribbons. a) 5 times reused Fe-A900 ribbons compared with Fe-AR ribbons. b) 5 times reused FeCu-A950 ribbons compared with FeCu-AR ribbons. Insets show a variation of Fe leaching concentrations by reused Fe-A900 and FeCu-A950 ribbons after 10 min and 30 min degradation, respectively (MB concentration: 20 ppm, H$_2$O$_2$ concentration: 1.0 mM, ribbon dosage: 0.5 g L$^{-1}$, pH 3.0, temperature: 25$^\circ$C). c-e) SEM images of 1$^{\text{st}}$, 2$^{\text{nd}}$ and 5$^{\text{th}}$ used Fe-A900 ribbons, respectively, after MB degradation. f-h) SEM images of 1$^{\text{st}}$, 2$^{\text{nd}}$ and 5$^{\text{th}}$ used FeCu-A950 ribbons, respectively, after MB degradation. All the SEM images correspond to zoom-in views of insets in Figure S9 (Supporting Information).
Figure 5. Schematic illustration. The structural and surface evolution of initialization and progress up to ~900°C annealing temperature in Fe-based glassy ribbons contributing to the reaction pathway in the Fenton process.
Short summary

Fully crystallized alloys gained by annealing of metallic glasses show excellent rejuvenated catalytic capabilities for ultrafast activation of peroxide. As self-motivated galvanic cells form in the fully crystallized alloys, a grain growth contributing to extensively reduced grain boundaries greatly weakens electron trapping and promotes inner electron transportation, providing a significant insight into exploit novel catalysts.

Keyword: metallic glasses, catalytic rejuvenation, crystallization, grain boundary, electron transfer

Compelling Rejuvenated Catalytic Performance in Metallic Glasses